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Memory Effect in Methane Hydrate Formation

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Memory Effect in Methane Hydrate Formation

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Abstract: Memory effect of formation water in methane hydrate formation and reformation is investigated in a high pressure reactor. Methane hydrate formation rates in fresh water and reacted water are measured at different pressures and temperatures. A significant reduction in formation time and incubation period is found with reused water. In the context of transportation of natural gas from distant gas fields as hydrate, this information can be utilized to reduce the transportation cost of natural gas.

1. Introduction

Methane hydrate is a clathrate. The word "clathrate" is derived from the Greek word "khlatron" meaning barrier, indicates crystalline inclusion compounds in which small guest atoms or molecules are physically trapped by three dimensionally shaped cavities formed by three dimensional assemblies of hydrogen atoms. [1] These compounds are called hydrates when the cage is formed from water molecules and gas hydrates when the enclosed molecules are gases. [2] The formation and decomposition of clathrate hydrates are first order phase transitions, not chemical reactions. Clathrate hydrates were first documented in 1810 by Sir Humphry Davy who found that water was a primary component of what was earlier thought to be solidified chlorine. [3]

According to size of the trapped molecule, three types of structures are commonly observed: cubic I, cubic II and hexagonal structure. These structures correspond to different arrangement of water molecules. [4] Structure formed by water molecules is determined by the size of guest molecules and composition of the mixtures. Common hydrate structures are shown in figure 1.
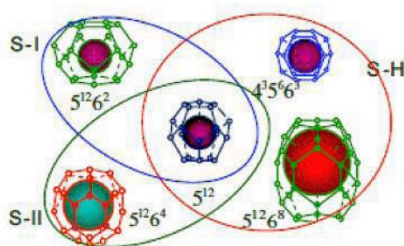

Figure 1. Molecular arrangements of different types of hydrate structures

The most common gas hydrate structures are SI and SII hydrates. SI has two types of cavity: a small pentagonal dodecahedral cavity consisting of 12 pentagonal rings of water molecules (20 water molecules) and a large tetrakaidecahedral cavity consisting of 12 pentagonal and two hexagonal rings of water molecules (24 water molecules).Structure II hydrate also has two cavity sizes, the pentagonal dodecahedral cavity and a larger hexakaidecahedral cavity consisting of 12 pentagonal and four hexagonal rings of water (28 water molecules). Unit cell of 7 (type H) consist of 34 water molecules, forming three types of cages, two small ones and one huge cage. In this case the unit cell consists of three small cages of 5^{12}; two small ones of type $4^{3}5^{6}6^{3}$ and one huge type of$5^{12}6^{8}$. The formation of type H requires the cooperation of two guest gases (large and small) to be stable.

Memory effect is a little studied phenomenon wherein water used for hydrate formation once appears to form hydrates faster when reused. The mechanism of memory effect is still imperfectly understood, some authors have suggested that the hydrate forming bonds may still be unbroken in the used water which facilitates the reformation later.

## 2. EXPERIMENTAL SETUP

2.1 MATERIALS

Methane gas with 99.5 % was used as guest molecule. Distilled water (host) was used to perform the experiments. Refrigeration test rig in the laboratory was modified to control the temperature inside the water bath. 99.5% pure methane gas was used in the experiments. The entire reactor was immersed in a constant temperature bath using a modified refrigeration setup as shown in figure 2.

Figure 2. Refrigeration rig modified to serve as the constant temperature bath.

2.2 The hydrate reactor

Stainless Steel 304 (SS-304) cylinder is the main part of the apparatus. SS 304 was selected because it can withstand high pressures and it would retain its properties even at low temperatures. [5] Monolithic piece of SS 304 was selected to avoid leakages due to weld and also to withstand high pressures. The reactor dimensions were such that it would have a total volume of 450 ml. Reactor's outer diameter was taken as 80mm, thickness is 10mm, and height of the cylinder was 90mm. The reactor is shown in the figure 3.
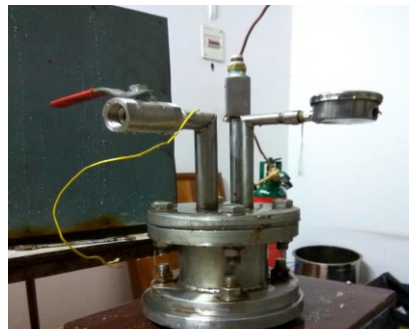

Figure 3. The high pressure hydrate reactor.

Figure 4. Pressure test with air compressor at IISC, Bangalore. Courtesy Prof. Kasturi Rangan

The reactor after fabrication by the authors was pressure tested successfully up to 20 Mpa at Indian Institute of Science, Bangalore with the help of Prof. Kasturi Rangan.

The reactor was immersed in the constant temperature bath as shown in figure 5.
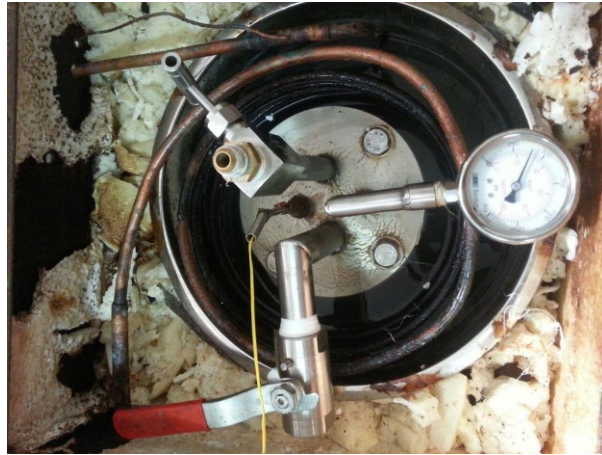
Figure 5. Reactor in the constant temperature bath.

The reactor was rinsed with de-ionized water once. The amount of water injected into the apparatus was 200ml for every experiment. The solution is then introduced into the cell through the ball valve. The air was removed from the reactor cell by charging compressed CH_4 into the reactor while keeping ball valve open. The ball valve is then closed to pressurize the apparatus to required level. The ends of thermocouple were connected to the temperature indicator. The experiment was started by placing the cell in a NaCl bath. The time taken for each degree fall in temperature inside the apparatus was noted. The higher limit of temperature was taken as 20°C. The pressure inside the apparatus decreased with decrease in temperature. At the time of hydrate formation there was a rise in temperature due to exothermic nature of methane hydrate formation. [8]

The temperature became steady at the point of hydrate formation. When the pressure of the reactor reached a constant value the gas hydrate formation was completed. After the temperature and the pressure in the apparatus became constant, the temperature and the pressure were noted as equilibrium data. [9] The thermocouple readings corresponding to hydrate formation for the pressure inside the apparatus was noted. Total time required for the formation of hydrate was also noted. The experiment was repeated by varying the pressure. The hydrate crystals formed is shown in figure 6.

Figure 6. Methane hydrate formed in the reactor.

3. Investigation of Hydrate Dissociation

The apparatus was placed outside the temperature bath (normal atmospheric conditions). The temperature was then gradually increased inside the apparatus. Time required for each degree raise in temperature is noted. Time required for completion of hydrate dissociation was also noted. The procedure was repeated for a different pressure. Different levels of dissociation of hydrate are shown in figures 7a to 7c.

Figure 7a. Dissociation of hydrate. 10 minutes after exposure to atmospheric pressure.

Figure 7b. Dissociation of hydrate. 15 mites after exposure.

Figure 7c. Dissociation of hydrate. 20 minutes after opening pressure vessel.

4. Investigation of Memory Effect

Memory effect refers to the strikingly shorter time required for hydrate formation when the water used has been previously used to form hydrates. When hydrates are decomposed and the resulting water is used to form hydrates, the formation is faster. No conclusive explanation has been given for this phenomenon, although one theory proposes that the very tiny hydrate crystals which may persist in the used water may be responsible by acting as seeds for hydrate formation.

Fresh water which was used for methane hydrate formation was reintroduced into the apparatus after the completion of the hydrate dissociation. When the experiment was repeated, the pressure inside the apparatus was found to decrease with decrease in temperature. [4]

Methane hydrate formation has been investigated at different pressures, and primary focus was on induction time, number of moles of methane consumed per moles of water and then water to hydrate conversion. After completion of hydrate formation the dissociation was done and the rise in pressure was noted. Memory effect investigation was performed with once hydrated water.

5. Results and Discussion

5.1 Memory Effect in Methane Hydrate Formation

Induction time and hydrate formation temperature during dissociation and formation of methane hydrate with memory water (water already used to form hydrate) was investigated at different

pressures. While using memory water hydrate formed at higher temperatures as compared to fresh water, but this trend was only observed at higher pressures. At lower pressure hydrate was formed at same temperature for memory water as that of fresh water. The time needed to form hydrate decreased while using memory water as compared to the time required for fresh water. The gas injected at high pressures remains at constant pressure for some time. Then with drop in temperature the pressure also falls. After the induction time there would be a sharp decrease in pressure for about 20-40 minutes. This is the period of methane hydrate formation. The sudden decrease in pressure shows the onset of methane hydrate formation. Then the pressure remains constant after the hydrate formation is completed. The time vs. pressure plot is shown in figure 8.
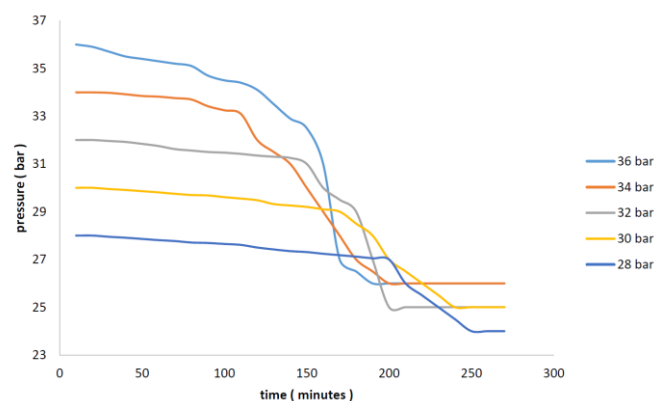

Figure 8. Time-pressure plot for Methane hydrate formation in memory water

Figure shown compares the time-pressure plots for methane hydrate formation at different pressures. The pressure drop is different at different conditions. Figure reveals that at high pressure the gas is easily soluble in water, so more number of methane moles get converted into hydrate, therefore pressure drop is high while at low pressure the solubility is low, so less number of methane moles get converted into hydrate, hence pressure drop is less. The time Vs temperature plot is shown in figure 9.
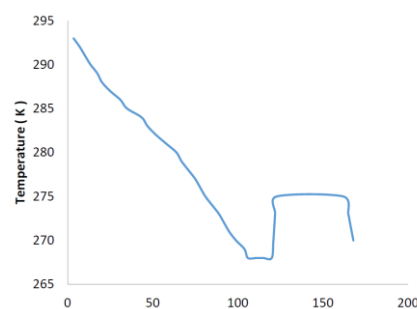

Figure 9. Time temperature plot of methane hydrate formation. X axis (Time) is in minutes.

Figure shows the Time-Temperature relation of methane hydrate formation at 36 bar. The temperature of the system is lowered using NaCl bath to 268 K. Temperature was reduced to 268 in order to keep the temperature well below the equilibrium point, which acts as a driving force for methane formation, known as under cooling. Therefore after the initial delay i.e. the induction time, temperature rises due to exothermic nature of methane hydrate formation. The experiment was continued till the temperature reaches steady state. This temperature was taken as methane hydrate formation temperature. The time Vs temperature plots at different pressures is shown in figure 10.
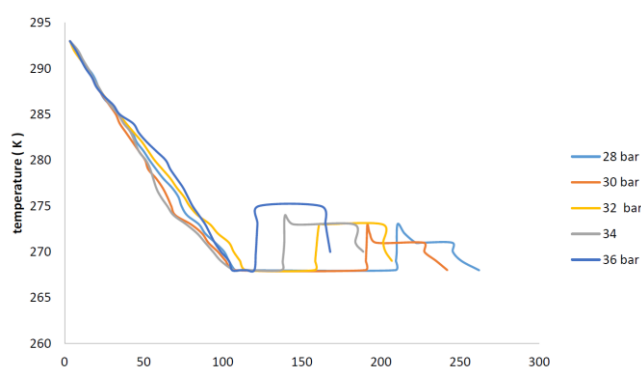

Figure 10. Time - temperature plot for different pressures. X axis is in minutes from introduction of methane.

Figure 10 shows time-temperature relation of methane hydrate formation at different pressures from 28 bar to 36 bar. It illustrates the variation in length of induction time with pressure and the exothermic nature of methane hydrate formation at different pressures.

The sudden rise in temperature, the plateau, and the subsequent drop in temperature are signatures of hydrate formation start and finish. The plot of number of moles of methane consumed Vs pressure is shown in figure 11.

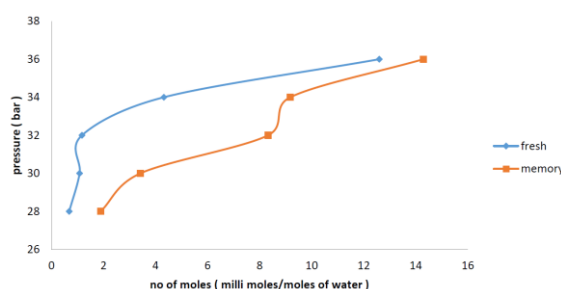### *5.2 Number of Moles Consumed*

Figure 11. Number of moles of methane hydrate consumed vs pressure.

Figure shows the comparison of number of moles consumed in memory water to moles consumed in fresh water. Usual trend is that number of moles consumed increases as pressure increases. But in memory water hydrate forms at higher temperature and the pressure drop is more as compared to the fresh water so number of moles consumed increases. Pressure Vs. temperature plots for both fresh and memory water are shown in figure 12.
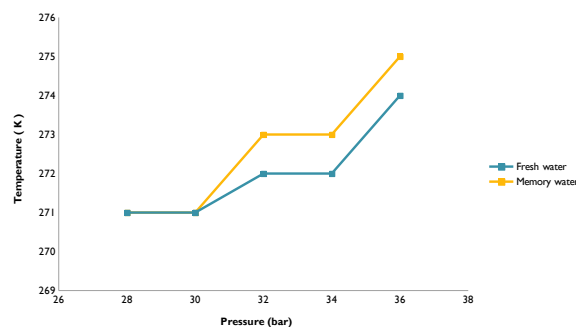
Figure 12: Pressure-Temperature relations for Methane Hydrate formation in memory water compared to pure water.

Results may be summarized as follows:

5.3 Hydrate Formation from Fresh water.

* As pressure increases the hydrate formation temperature increases.

* Induction time decreases with increase in pressure.

* As hydrate formation starts there would be a sudden decrease in pressure.

* Hydrate formation is exothermic in nature.

* Number of moles consumed increases as pressure increases.

* Water to hydrate conversion rate is higher in higher pressure range.

5.4 Hydrate Formation from Memory water.

* Hydrate formation shows an increase in formation temperature at higher pressure, but at lower pressure there is no discernible effect on formation temperature.

* Induction time reduces (12.9% of total time) in memory water as compared to fresh water (25%).

* The pressure drop is greater as compared to fresh water.

* Number of moles of CH_4 consumed in memory water is more as compared to fresh water.

* Water to hydrate conversion rate is also high.

5.5 Hydrate dissociation below 20°C.

* Hydrate dissociation temperatures are closer to hydrate formation temperatures.

* Hydrate formed at higher pressures can exist undissociated for more time in atmospheric conditions as compared to lower pressure conditions.

5.6 Hydrate dissociation above 25°C.

* Hydrate dissociated water when kept for long time at ambient temperature, its temperature would rise above 25°C and there is no significant memory effect for this water.

* Hydrate formed in this condition was similar to fresh water, temperature of hydrate formation was exactly similar, but time varied, showing that induction time for methane hydrate formation is stochastic.

6. CONCLUSION

Experimental investigation on methane hydrate formation in fresh water was conducted and it was compared with the formation in memory water. The induction time, temperature for hydrate formation, pressure drop during hydrate formation and exothermic nature of methane hydrate formation was studied.

It was found that the formation temperature is higher when forming hydrate with previously used (memory) water.

A significant drop in induction time was found to exist when forming hydrate with previously used (memory) water. (12.9% Vs 25%). This effect disappears when the used water is brought above 25°C.

The rate of hydrate formation is found to be 10 times higher in memory water as compared to fresh water. The number of moles of methane consumed is also found to be 10.5 times more as compared to fresh water.

Conflict of interest disclosure

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgment

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